Shock barometer using cathodoluminescence of alkali feldspar

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[1] Color cathodoluminescence (CL) images of unshocked and experimentally shocked sanidine at pressures up to 40.1 GPa showed red-violet emission below 20.0 GPa and blue emission above 20.0 GPa. The phases in these shock-recovered samples were identified as crystalline feldspar for red-violet emitting areas and as diaplectic feldspar glass for blue emitting ones by micro-Raman spectroscopy. CL spectra of these shocked sanidine have emissions at ~330, ~380 and 400–420 nm of which intensities increase with an increase in shock pressure. Similar UV-blue emissions were found in alkali feldspar and the glass in Martian meteorites and Ries crater impactite. The deconvolution of these CL spectra provides the emission component at 2.948 eV assigned to shock-induced defect center, where this intensity correlates linearly with peak shock-induced pressure on sanidine, with little dependence on composition and structure. The correlation gives quantitative values of the shock pressures experienced by the feldspar, resulting in estimated shock pressures of Martian meteorites and Ries crater impactite. The CL intensity of feldspar has a potential for a universal shock barometer with high spatial resolution (~1 µm) and in a wide pressure range (theoretically ~4.5–40.1 GPa). This leads to a breakthrough in understanding the impact histories on Earth, Moon, and Mars.


1. Introduction

[2] Meteorite and impactite that have experienced impacts provide vital information on collision and accumulation processes of asteroid and planetesimal during planetary accretion, formation process of impact crater on planets and their satellites, and ejection process from the parent body [e.g., Stöffler et al., 1991; French, 2004; Beck et al., 2005; Ohtani et al., 2010]. Materials subjected to shockwaves display characteristic and irreversible structural changes on both macroscopic and microscopic scales, depending on the applied shock strength. The shock pressure is one of the most important parameters that need to be clarified in the collisional history of asteroid, meteorite and planetesimal impacts [e.g., Stöffler et al., 1991; Fritz et al., 2005a; Gillet et al., 2007; Kubo et al., 2010]. Various techniques such as refractive index, X-ray diffraction, infrared (IR) absorption and micro-Raman spectral analyses, as well as optical microscopic observations, have been applied to evaluate the shock pressure in minerals, predominately feldspar, which is one of major rock-forming minerals on the surfaces of Earth, Moon, and Mars. The shock pressures on meteorites and impactites have been qualitatively estimated based on the presence of characteristic features, structures or phase and on the paragenetic assembly of high-pressure phases [e.g., Stöffler et al., 1986; Ostertag et al., 1986; Beck et al., 2005; Fernandes et al., 2009; El Goresy et al., 2010a; Ohtani et al., 2010]. Although X-ray diffraction analysis and IR spectroscopy of shocked feldspar have been conducted for usage as a shock barometer, they are not enough to estimate shock pressure on feldspar because the change of their features depends on many factors such as the shock-induced pressure, phase composition, the degree of Si–Al order, and grain size [Hass et al., 1978]. Raman spectroscopy combined with optical and scanning electron microscopes has been used to identify micrometer-order feldspar and maskelynite (an amorphous product changed from shocked feldspar) and to deduce briefly the degree of shock strength in Martian meteorites and impact crater [Fritz et al., 2005a]. The refractive index measurement also gives quantitatively estimated shock pressure on a few hundred micron-order feldspar grains in meteorite and impactite in the range from ~15 to 45 GPa [Lambert, 1981;
2.1. Shock Experiment

They were cut and polished into flat discs (8-mm diameter, 1-mm thickness) and enclosed in 304 stainless steel container (30-mm diameter × 30-mm length). The sample disc was set 3 mm inside from the impact surface. A propellant gun with a 30-mm bore at the National Institute for Materials Science [Sekine, 1997] was employed to accelerate a projectile, with a metal flyer (29-mm diameter × 3-mm thickness, Al alloy for the 10 GPa shot and stainless steel 304 for the other shots), to a required velocity. The shock pressures produced in samples are assumed to reach an equilibrium, judging from a thickness of the flyer against the samples, with that of the container due to shock wave reverberation within container, and were determined using the impedance match method from the measured velocity of projectile and the known Hugoniot [Sekine, 1997; Yamaguchi and Sekine, 2000]. Detailed information on shock experiments is followed from Yamaguchi and Sekine [2000]. The impact velocities of flyer, and hence peak shock pressures induced on sanidine were set at 0.857 km/s and 10.0 GPa (named as Sa10), at 0.958 km/s and 20.0 GPa (Sa20), at 1.423 km/s and 31.7 GPa (Sa30), and at 1.730 km/s and 40.1 GPa (Sa40), as well as microperthitic microcline with albite at 1.47 km/s and 33.0 GPa (Mi30 and Ab30, respectively). These shock-recovered samples and unshocked sample (named as Sa00) were embedded on the slide glass with non-luminescent epoxy resin, and were polished and mirror-finished using 1 μm diamond abrasive compound for CL and Raman spectroscopy. X-ray diffraction analysis was carried out for their powder samples which were fixed on quartz plate to detect an X-ray diffraction pattern of amorphous phase in experimentally shocked samples.

2.2. Meteorite and Impactite

In this study, CL of experimentally shocked alkali feldspar has been measured to characterize their emission mechanisms and to clarify the shock-induced effect on their CL signals, and then the results have been applied to estimate the shock pressure of alkali feldspar in Martian meteorites of shergottite in nakhlite of Yamato 000749 (Or70Ab27An3) (allocated to 45 GPa, judging from the presence of maskelynite). Information on these Martian meteorites and impactite in the present study is summarized as follows:

1. NWA 2975 (basaltic shergottite) has glass pockets and vesicular black glass veins with maskelynite (An35) entirely converted from plagioclase by shock metamorphism [Wittke et al., 2006; Bunch et al., 2008], implying NWA 2975 experienced shock metamorphism. No quantitative estimation of the shock pressure has been reported up to now. According to Fritz et al. [2005a], most shergottites including in NWA 2975 experienced shock pressure in the range of 30 to 45 GPa, judging from the presence of maskelynite.

2. Shergotty (basaltic shergottite) contains several types of high-pressure phases such as maskelynite, dense silica glass, post-stishovite, and possibly stishovite formed by shock on the meteorites [Tscherneck, 1872; Sharp et al., 1999; Chen and El Goresy, 2000; El Goresy et al., 2000, 2010a]. Shergotty is the type specimen for maskelynite [Bunch et al., 2008]. The shock pressure has been estimated...
to be at 29 GPa with a post-shock temperature of 200°C as determined by the existence of maskelynite [Stöffler et al., 1986]. The refractive index measurement on the maskelynite gives an estimation of the shock pressures at 30.5 ± 2.5 GPa [Fritz et al., 2005a]. According to Fritz et al. [2005b], Shergotty was not subjected to heating at a temperature higher than 630°C after the release from shock compression, judging from an annealing experiment, refractive index measurement and Raman spectroscopy of experimentally shocked anorthite glass reported by Reynard et al. [1999]. The peak shock pressure of Shergotty, however, was evaluated to be higher than 40 GPa and as high as 90 GPa [Sharp et al., 1999; El Goresy et al., 2010a].

[10] 3. Dhofar 019 (basaltic shergottie) has characteristic shock features such as fracturing, mosaicism and rarely impact-melt pocket, consisting of olivine with planer fractures, pyroxene with polysynthetic mechanical twins and maskelynite converted from plagioclase. Shock pressure is evaluated in the range of 30–35 GPa as determined by the features in these shocked minerals [Budijok et al., 2001]. Partially birefringent plagioclase and maskelynite led to shock pressures of 26–29 GPa [Fritz et al., 2005a].

[11] 4. Zagami (basaltic shergottie) contains thin, vesicular veins and pockets of black glass produced by shock metamorphism [McCoy et al., 1992; Langenhorst and Poirier, 2000]. It is further characterized as containing high-pressure phases such as omphacite and hollandite-type KAlSi3O8. Stishovite and post-stishovite SiO2 also occur as the high-pressure phases with shocked textures gives the estimated shock pressure at 31 GPa and peak temperature at 220°C [Stöffler et al., 1986]. The shock pressure and the post-temperature were also deduced at >22.5 GPa and >2250 K [Beck et al., 2006], based on subsolidus and melting experiments of a K-rich basaltic composition reported by Wang and Takahashi [1999]. Refractive index method on maskelynite provided shock pressures at 27 GPa [Lambert, 1985], 29.3 GPa [Langenhorst et al., 1991], 30 GPa [Langenhorst and Poirier, 2000], and 29.5 ± 0.5 GPa [Fritz et al., 2005a].

[12] 5. Yamato 000749 (nakhlite) and the paring meteorite (Yamato 000593) have the mesostasis including lath-shaped plagioclase, of which Raman spectra and reflective index provide shock pressure in the range of 5–14 GPa [Fritz et al., 2005a].

[13] 6. The Ries Crater has been established as a complex meteorite impact crater by the discovery of the high-pressure phases such as coesite, stishovite [Showemaker and Chao, 1960, 1961; Chao and Littler, 1963], jadeite [James, 1969], diamond [El Goresy et al., 2001], baddeleyite-type TiO2 [El Goresy et al., 2001, 2010b], columbite-type TiO2 [James, 1969], and LiNbO3-type FeTiO3 [Dubrovinsky et al., 2009]. Recent studies indicate better constraints for pressure estimation for the suevite, being in a wide range of pressure of <22 GPa and at a peak temperature of >1000°C and a post-shock temperature of <500°C [El Goresy et al., 2010b]. Suevite in Ries crater contains the minerals metamorphosed at various shock stages, and consists of 8% unshocked or relatively low shocked clasts (<10 GPa), 34% shocked ones at 10–35 GPa (stage I), 30% shocked ones at 35–45 GPa (stage II), and 27% heavily shocked ones at 45–60 GPa (stage III), respectively [Engelhardt, 1997]. The shock pressures on amphibolite in Ries crater were also estimated to be at 20–22 to 28–34 GPa (stage Ia) and 28–34 to 42–45 GPa (stage Ib), judging from occurrence of the shock veins [Stöffler and Grieve, 2007]. Furthermore, Si contents of majorities in the shocked amphibolite give a deduction of shock pressure at ~15–17 GPa and temperature at ~2150–2230°C [Stähle et al., 2011].

2.3. Analytical Methods

[14] A scanning electron microscopy-cathodoluminescence (SEM-CL) analysis was conducted to measure CL spectra ranging from 300 to 800 nm in 1 nm steps using an SEM (JEOL: JSM-5410) combined with a grating monochromator (Oxford: Mono CL2) at the Okayama University of Science. The CL emitted from each sample was collected by a retractable parabolic mirror coated with aluminum (collecting efficiency of 75%) and was dispersed by a grating monochromator, which has the following characteristics: 1200 grooves/mm, a focal length of 0.3 m, F of 4.2, limit of resolution of 0.5 nm, and slit width of 4 mm at the inlet and outlet. The CL signal was recorded by a photon counting method using a photomultiplier tube (Hamamatsu: R2228). All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp [Ikenaga et al., 2000; Kayama et al., 2009b]. This correction prevents errors in the peak position of emission bands and allows quantitative evaluation of CL intensity. Detailed construction of the equipment and analytical procedure can be followed from Ikenaga et al. [2000]. According to the method proposed by Stevens-Kalceff [2009] and Kayama et al. [2010], the corrected CL spectra in energy units were deconvoluted into Gaussian components corresponding to each emission center using the peak-fitting software (Peak Analyzer) implemented in OriginPro 8J SR2. The number of Gaussian components was determined by chi-square test for each CL spectral datum of measured samples fitted with the smallest margin of standard error. For more details on the analytical procedures of CL spectral deconvolution, refer to Kayama et al. [2010]. Pseudocolor CL images were captured by a ChromaCL imaging detector (Gatan) combined with SEM-CL system. The ChromaCL system operates using the principles of efficient light collection from the specimen and dispersion onto an array detector (Gatan: multiarray PMT detector). All CL measurements were performed at 15 kV accelerating voltage and 2.0 nA beam current in a scanning mode.

[15] The laser Raman spectroscopy was carried out using a NRS-2100 (JASCO) at Kyoto University with an Ar laser of 514.5 nm wavelength. The measured laser power was 100 mW on the sample with a ~1 μm spot size. The signal diffracted by a 2400 lines/mm grating was collected using a cooled CCD detector at ~70°C. Raman spectra were measured in five accumulations of 30 s each in the range of 120 to 1650 cm⁻¹ in steps of 1 cm⁻¹. Raman bands were calibrated by monitoring the position of the O-Si-O bending vibration (464 cm⁻¹) in reference standard quartz with high optical grade before and after the measurements, and the analytical reproducibility was found to be less than 1 cm⁻¹.

3. Results

3.1. Color CL Microscopy

[16] Color CL image of unshocked sanidine (Sa00) indicates a red-violet emission with homogeneous distribution of
the intensity (Figure 1a). A red-violet CL emission was also observed in color CL image of Sa10 (Figure 1b). Sa20, however, displays a bright blue CL emission (area b in Figure 1c) with vein-shaped textures with a dull red-violet luminescent matrix (area a in Figure 1c). Optical microscopic, SEM and BSE images have no feature corresponding to distributions of the CL intensity and color in the images of Sa20. A blue emission is also distinguished in the color CL images of Sa30 and Sa40 (Figures 1d and 1e). Color CL microscopy revealed a water blue emission in unshocked microcline and a red one in unshocked albite, whereas bright blue emissions were commonly obtained from color CL images of Mi30 and Ab30.

Figure 1. Color cathodoluminescence images obtained from (a) unshocked and experimentally shocked sanidine at (b) 10.0 GPa, (c) 20.0 GPa, (d) 31.7 GPa, and (e) 40.1 GPa. Unshocked and shocked sanidine (the recovered samples at 10.0 GPa and 20.0 GPa in area a) show red-violet CL emissions, whereas diaplectic feldspar glasses (the recovered samples at 20.0 GPa in area b, 31.7 GPa, and 40.1 GPa) show bright blue emissions. Crosses mean measuring points of the Raman and CL spectra shown in Figures 2 and 4, respectively.
samples, while the peaks are slightly broadened with an increase in shock pressure (Figure 3). On the other hand, Sa30 and Sa40 present amorphous pattern in 2θ range of 22–25 degree and no sharp diffraction peaks.

3.4. CL Spectroscopy

[21] The CL spectrum of Sa00 shows a blue emission band at ~410 nm and a red-IR one at ~730 nm (Figure 4). Sa10 has a blue emission at ~420 nm, of which the intensity is higher than that of Sa00. A Red-IR emission at ~720 nm is also observed in CL spectrum of Sa10. CL spectrum of Sa20a consists of emission bands at ~400 and ~715 nm in blue and red-IR region, respectively. With increasing shock pressure, the peak wavelength of the red-IR emission at ~730 nm for Sa00 shifts to ~720 nm for Sa10 and to ~715 nm for Sa20a. The CL spectrum of Sa20b shows a blue emission band at ~380 nm with higher intensity than that of the blue emission at ~400 nm in Sa20a. An emission band at ~330 nm is also found in CL spectrum of Sa20b, but not in those of Sa00, Sa10 and Sa20a. On the other hand, the red-IR CL emission is undetectable in Sa20b. The CL spectra of Sa30 and Sa40 consist of emission bands at ~330 and ~380 nm. The intensities of all UV-blue emissions increase with increasing shock pressure. Similar UV-blue emissions at ~330 and ~380 nm are found in CL spectra of Mi30 and Ab30.

[22] The CL spectra of Sh, NW and Zg have emission bands at ~330 and ~380 nm in UV-blue region, where the intensities of both emission bands are highest in Sh followed by NW and then Zg. Similarly, Sa30 and Sa40 have UV-blue emission bands at ~330 and ~380 nm with higher CL intensities than those of Sh, NW and Zg. The CL spectra of Dh and Rs also show emission bands at ~330 and 380 nm, with lower intensities than the corresponding bands in other shergottite. A red-IR CL emission is undetectable in alkali feldspar in the shergottite, but detectable at 715 nm in Rs, similar to Sa20a. The CL spectrum of Ym represents an emission band at ~420 nm in blue region, and the intensity is lower than those of the UV-blue emissions in alkali feldspar in the shergottite and the impactite. A red-IR emission at 730 nm is also found in the CL spectrum of Ym.

4. Discussion

4.1. Experimentally Shock-Induced Effects on CL

4.1.1. Color CL Characteristics

[23] CL color of the recovered samples varies depending on shock-induced pressure (Figure 1). X-ray diffraction analysis revealed that Sa00, Sa10 and Sa20 have a characteristic diffraction pattern of sandine structure with pronounced peaks, whereas those of Sa30 and Sa40 show non-crystalline patterns, which have been observed in diaplectic glass of alkali feldspar [Hass et al., 1978]. Raman spectra of Sa00, Sa10 and Sa20a consist of pronounced peaks at ~180, 290, 470–490 and 510 cm$^{-1}$ (Figure 2), which are assigned to the compression vibration of four-member tetrahedral rings [McKeown, 2005]. Raman spectra of Sa20b, Sa30 and Sa40, however, exhibit weak and broad peaks at ~510 and 600 cm$^{-1}$ (Figure 2), which are similar to Raman spectral pattern of diaplectic feldspar glass and maskelynite, known as shock metamorphism of plagioclase [Fritz et al., 2005b; Kayama et al., 2009a]. These observations suggest that strong shock
metamorphism destroys a linkage of T–O–T bond in the framework structure of sanidine, resulting in transition of sanidine into diaplectic feldspar glass. Raman spectroscopy and X-ray diffraction analysis revealed that blue emitting areas in the recovered samples are identified as diaplectic feldspar glass, but red-violet areas are identified as shock feldspar. Sa20 consists of partly vein-shaped diaplectic feldspar glass with bright blue CL and almost shock feldspar as red-violet luminescent matrix (Figure 1c). Sa30 and Sa40 with blue CL completely transformed to diaplectic feldspar glass by shock, whereas Sa10 can be identified to be shock feldspar.

4.1.2. Emission Centers

[24] CL spectrum of Sa00 shows a red-IR emission at 730 nm, which is attributed to Fe$^{3+}$ substituting for Al$^{3+}$ tetrahedral sites [Finch and Klein, 1999; Götz et al., 2000; Lee et al., 2007]. The shocked sanidine also has a red-IR emission band at 720 nm for Sa10 and 715 nm for Sa20a (Figure 4). Similar peak shifts have been reported in Mn$^{2+}$ impurity center in experimentally shocked plagioclase [Kayama et al., 2009a]. Shock pressure makes an alteration of coordinate configuration around Mn$^{2+}$ ions accompanied with a decrease in the strength of its crystal field, which causes a peak shift of the yellow CL emission in plagioclase. The peak shifts of the red-IR emission, therefore, occur due to a structural change in sanidine by shock and the subsequent alternation in the crystal fields. The red-IR emissions are, however, undetectable in CL spectra of Sa30 and Sa40. A similar decrease in intensity at high shock pressures has

Figure 3. X-ray diffraction patterns of (a) unshocked and experimentally shocked sanidine at (b) 10.0 GPa, (c) 20.0 GPa, (d) 31.7 GPa, and (e) 40.1 GPa.
been observed in CL of shocked plagioclase activated by Mn2+ impurity center [Kayama et al., 2009a]. It is noteworthy that the drastic decrease in intensity of the red-IR CL emission can be explained by a change of Fe3+ impurity center into non-luminescence center due to a destruction of linkage related to Fe3+-O–T bonds, which leads to absence of a red-IR emission band in diaplectic feldspar glass.  

[25] The blue emission at ~410 nm is found in CL spectrum of Sa00 (Figure 4), and is assigned to Ti4+ impurity center and to oxygen defect center associated with Al-O-Al and Al-O-Ti bridges (Al-O-Al/Ti defect center) [Finch and Klein, 1999; Götzke et al., 2000; Lee et al., 2007; Kayama et al., 2010]. The peak wavelength is, however, centered at ~420 nm for Sa10, at ~400 nm for Sa20a, and at ~380 nm for diaplectic feldspar glass of Sa20b, Sa30 and Sa40, suggesting different type of emission centers between unshocked and the recovered sanidine. An emission band at 330 nm is also recognized in CL spectra of the diaplectic feldspar glass. With increasing shock pressure, the intensities of these UV-blue emission bands in the recovered samples increase (Figure 4), implying formation of several shock-induced emission centers related to these UV-blue emissions in shocked sanidine and the diaplectic feldspar glass. The increase of CL intensity in UV-blue emissions and the decrease in red-IR one with an increase in shock pressure give a change from a red-violet CL color in shocked sanidine into blue color in diaplectic feldspar glass under CL microscopy.

4.1.3. Shock-Induced Defect Centers  

[26] A spectral deconvolution was carried out for CL data obtained here using the peak-fitting method proposed by Stevens-Kalceff [2009] and Kayama et al. [2010] to characterize CL properties of the shock-induced defect centers. The deconvoluted CL spectrum of Sa00 can successfully separate the blue emission band into two Gaussian components centered at 3.048 eV (±0.008 eV) and at 2.822 eV (±0.015 eV) (Figure 5a), where the former is attributed to Ti4+ impurity and the latter to Al-O-Al/Ti defect centers [Kayama et al., 2010]. The deconvoluted CL spectrum of Sa10 provides two components at 2.822 eV and 2.948 (±0.029) eV, whereas the component at 3.048 eV was undetected (Figure 5b). Sa10 has a lower intensity at 2.822 eV than Sa00. Similar phenomena have been recognized in blue CL of experimentally shocked plagioclase [Kayama et al., 2009b], where CL intensities of blue emission assigned to Ti4+ impurity and Al-O-Al/Ti defect centers decrease with increasing shock pressure. The blue CL assigned to these centers seems to be quenched due to an increase in the population of non-radiative transition, like the case of Fe3+ impurity center described above. Although the deconvoluted CL spectrum of Sa20a consists of two components at 2.948 eV and 3.263 (±0.056) eV (Figure 5c), diaplectic feldspar glasses in Sa20b, Sa30 and Sa40 have the components at 2.948, 3.263 and 3.881 (±0.014) eV (Figures 5d, 5e and 5f). The component at 2.822 eV was not observed in the recovered samples at shock pressures above 20 GPa, suggesting a destruction of linkage of Al-O-Al and Al-O-Ti bridges accompanied with shock-induced transition of sanidine into diaplectic feldspar glass. The components at 3.263 and 3.881 eV are detected in only the samples of Sa20b, Sa30 and Sa40, which are characteristic CL signals of diaplectic feldspar glass. On the other hand, the emission component at 2.948 eV can be assigned to the shock-induced defect centers in both shocked feldspar and diaplectic feldspar glass.

4.1.4. Relationship Between CL Intensity and Shock Pressure  

[27] The intensities of the components at 2.948, 3.263 and 3.881 eV increase with an increase in shock pressure (Figure 6 and Table 1). It is worth noticing that Sa20a has the same level of emission intensity at 2.948 eV as Sa20b, within experimental errors, regardless of the phase difference between them. This fact implies that there is no relationship between a formation of the shock-induced defect center related to this component and a destruction of linkage of T-O-T bond due to shock metamorphism. The components at 2.948, 3.263 and 3.881 eV are also detected in the deconvoluted CL spectra of Mi30 and Ab30, of which the intensities at 2.948 eV are comparable to that of Sa30 (at 31.7 GPa), despite the fact that the composition and structure ordering differ among the feldspar as these starting materials (Figure 6 and Table 1). This suggests that feldspar behave similarly in terms of the density of the shock-induced defect center at 2.948 eV against shock pressure, even though they have different mineralogical features. The component intensity or the defect density, therefore, depends on shock metamorphic effect, but little on the other factors.

[28] Figure 6 illustrates the relationship between shock pressure and the intensity at 2.948 eV, which appears to be linear at pressures up to 40.1 GPa. Such a linear correlation has been also known between CL intensities and concentration of Mn2+ impurity center in plagioclase or radiation dose in albite [Götzke et al., 2008]. These results indicate that the approximation method varies depending on type of emission center. Although the plot in Figure 6 has CL data related to the intensity at 2.948 eV for only five samples (Sa10, Sa20a, Sa20b, Sa30 and Sa40), a linearity can be assumed to get a simple relationship between the intensity and shock pressure in order to use as a shock barometer for meteorite and impactite.
4.2. Applications to Martian Meteorites and Impactite

4.2.1. Luminescent Visualization of Shock Effect

CL and Raman spectroscopy revealed that alkali feldspar in the shergottite and the impactite, emitting bright blue CL, indicate rather weak Raman peaks at 510 and 600 cm⁻¹, whereas that in the nakhlite, having red-violet CL, shows pronounced peaks at ~180, 290, 485 and 510 cm⁻¹ (Figure 2). CL spectra of alkali feldspar in the shergottite exhibit emission bands at ~330 and 380 nm, similar to those of Sa20b, Sa30 and Sa40 (Figure 4). CL spectrum of Rs has a UV-blue CL emission at ~380 nm and a red-IR one at ~715 nm, but that of Ym consists of blue one at ~420 nm and red-IR one at ~720 nm. These results imply that alkali feldspar in the shergottite and the impactite were identified as dialectric feldspar glass, but that in the nakhlite as shock feldspar. Thus, CL microscopy and spectroscopy allow us to visualize shock metamorphic effect on

Figure 5. Deconvoluted cathodoluminescence spectra of unshocked and experimentally shocked sanidine in energy unit. The deconvolution for (a) unshocked and experimentally shocked sanidine at (b) 10 GPa, (c, d) 20.0 GPa in area a and area b, respectively, (e) 31.7 GPa, and (f) 40.1 GPa can be separated into several Gaussian components as illustrated. Integral intensities of these components are summarized in Table 1.
micrometer-ordered feldspar and the glass as high-spatial resolution color CL imaging.

4.2.2. Quantification of Shock Pressure

[30] The deconvolution of CL spectra obtained from alkali feldspar in the shergottite provides the same three components at 2.948, 3.263 and 3.881 eV (Figure 7) as those in the recovered samples (Figure 5). The component at 2.948 eV was also detected in the deconvoluted CL spectra of alkali feldspar in the nakhlite and the impactite (Figure 7). Using the linear correlation in Figure 6, one can estimate quantitatively shock pressures for alkali feldspar in the meteorites and the impactite. Table 2 lists the estimated values, and we compare them with the values reported by the previous studies, as listed in Table 2. The results are consistent with the previous estimation using refractive index method and Raman spectroscopy. Although the conventional methods cannot give us quantitative evaluation of shock pressure for a grain with micron size or very limited amount of meteorite such as NWA 2975, the shock pressure on NWA 2975 has been deduced successfully by the present method for the first time. The present CL spectroscopy of alkali feldspar in Yamato 000749 also allows us to estimate a shock pressure of 7.4 ± 0.8 GPa, while the conventional methods provide only dispersed values for a weakly shocked meteorite such as nakhlite. The peak wavelengths of red-IR emission assigned to Fe$^{3+}$ impurity center are centered at 730 nm for Ym, similar to Sa00 and at 715 nm for Rs, similar to Sa20a, which deduces shock pressure below 10.0 GPa for

Table 1. Integral Intensities of Gaussian Components for Unshocked Sanidine (Sa00), Experimentally Shocked Sanidine at 10.0 GPa (Sa10), at 20.0 GPa With Red-Violet (Sa20a) and Blue Emissions (Sa20b), at 31.7 GPa (Sa30) and at 40.1 GPa (Sa40), Experimentally Shocked Microcline at 33.0 GPa (Mc30), Albite at 33.0 GP (Ab30) and Alkali Feldspar in Yamato 000749 (Ym), in Zagami (Zg), in Dhofar 019 (Dh), in Shergotty (Sh), in NWA 2975 (Nw) and in the Amphibolite From Ries Crater (Rs), Where the Intensities of Each Component Were Derived From the Averages of Thirty Measured CL Spectra for Each Sample of the Shock-Recovered Feldspar, and From Those of Five Ones for an Alkali Feldspar Grain in the Martian Meteorites and the Impactite

<table>
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<th>Component</th>
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<th>Sa20A</th>
<th>Sa20B</th>
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<th>Sa40</th>
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<th>Ym</th>
<th>Zg</th>
<th>Dh</th>
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<td>3.048 eV</td>
<td>258</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>647</td>
<td></td>
</tr>
<tr>
<td>3.263 eV</td>
<td></td>
<td>241</td>
<td>696</td>
<td>1708</td>
<td>2601</td>
<td>4569</td>
<td>4676</td>
<td>263</td>
<td>126</td>
<td>743</td>
<td>676</td>
<td>1424</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.881 eV</td>
<td></td>
<td>432</td>
<td>1262</td>
<td>1419</td>
<td>2010</td>
<td>3793</td>
<td>128</td>
<td>620</td>
<td>209</td>
<td>959</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Intensity of components is expressed as a.u.*

Figure 6. Correlation plot of integral intensities of Gaussian components at 2.948, 3.263, and 3.881 eV against shock pressures on shock-recovered sanidine (Table 1 lists actual data), where the standard deviations were obtained from thirty measured CL spectra for each sample. The intensities at 2.948 eV with the standard deviations are also plotted for experimentally shocked microcline and albite at 33.0 GPa. The relationship between the intensity at 2.948 eV and shock pressure, as indicated by a gray line, gives a quantitative shock barometer.

Figure 7. Deconvoluted cathodoluminescence spectra of alkali feldspar in Martian meteorites and impactite. Samples are alkali feldspar in the Martian meteorites, NWA 2975, Shergotty, Dhofar 019, Zagami, and Yamato 000749, and in amphibolite of the drilling core samples at depth 601–602 m from the surface in the center of Ries Crater. The intensities of the deconvoluted Gaussian components are listed in Table 1.
4.2.3. Validation of Shock Barometer Using CL

Table 2. Shock Pressures on Martian Meteorites of Dhofar 019, Shergotty, Zagami, NWA 2975 and Yamato 000749 and on the Amphibolite From Ries Crater Evaluated by the Present Cathodoluminescence Spectroscopy and a Comparison With the Reported Data Using the Other Techniques (av. = average)

<table>
<thead>
<tr>
<th>Samples</th>
<th>This Study (CL Intensity)</th>
<th>Previous Studies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>26–32 (av. 28.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29 ± 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30.5 ± 2.5</td>
</tr>
<tr>
<td>NWA 2975</td>
<td>34.4 ± 2.0 GPa</td>
<td></td>
</tr>
<tr>
<td>Shergotty</td>
<td>31.3 ± 1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>26–29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>Dhofar 019</td>
<td>26.1 ± 1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31 ± 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>28–30 (av. 29.2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Zagami</td>
<td>25.5 ± 1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>29.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Yamato 000749</td>
<td>7.4 ± 0.8</td>
<td>5–14</td>
</tr>
<tr>
<td></td>
<td>5–20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20–22 to 28–34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>28–34 to 42–45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~15–17</td>
<td></td>
</tr>
<tr>
<td>Ries crater</td>
<td>15.9 ± 0.7</td>
<td></td>
</tr>
</tbody>
</table>

*The standard deviations were obtained from five CL spectra of each sample.

Yamato 000749 and in a range of 10–20 GPa for the Ries crater impactite. These values are concordant with those evaluated by the present CL spectral deconvolution method. According to the linear approximation shown in Figure 6, the minimum applicable pressure will be down to a pressure of ~4.5 GPa. This validation will be discussed in next section in detail. Accordingly the CL spectral deconvolution for alkali feldspar proposed in this study can be used as a novel and quantitative shock barometer for a wide range of pressures (4.5–40 GPa) with high spatial resolution (~1 μm), even though the details of mineralogical features such as chemical composition and structure are not known, implying an application of the shock estimation for an alkali feldspar grain with micron size in the precious and small amount of meteorites, as well as micrometeorites from stardust and asteroid.

4.2.3. Validation of Shock Barometer Using CL

[31] The linear approximation for alkali feldspar has a sufficient potential for a quantitative shock estimation as described above, whereas the following problems should be solved for more precious and reliable improvement: (1) assumption of linear approximation; (2) the extrapolation below 10.0 GPa; (3) concordance and discordance with shock pressures estimated by previous studies; (4) difference between single shock loading and shock reverberation experiments; (5) post-temperature effect.

[32] A plot of the intensity at 2.948 eV against shock pressure on the sanidine is linear (Figure 6) and the shock pressures estimated for several natural samples using this relation are consistent with those reported by previous studies (Table 2). It also indicates that the linearity is sufficiently reliable, although there is significant difference in shock duration, rising, and probably temperature between the conditions of experimental and natural impacts. Further shock experiments will be needed to obtain more precious and reliable calibration in order to make clear such difference.

[33] The linear approximation is extrapolated down to ~4.5 GPa (Figure 6), which has been judged from the CL spectral measurements at various beam currents. CL spectroscopy of shock-recovered sanidine at 2.0, 5.0 and 10.0 nA gives us the linear approximations with different gradient, of which intersections at the pressure axis appear to be converged at ~4.5 GPa regardless of different beam currents. The intersection obtained from the measurements below 1.0 nA, however, tends to shift to high shock pressure side with a decrease in beam current. This might be explained by either production of shock-induced defect center related to the component at 2.948 eV above ~4.5 GPa or detection limit by the present SEM-CL. In each case, this fact suggests the validity of linear extrapolation down to 4.5 GPa. This lower limit of the shock estimation obtained from the extrapolation is, however, just a practical value, and understandably we need further shock experiments below 10 GPa and further CL spectral analysis using more sensitive CL instruments than the present SEM-CL to improve precision and reliability of the shock estimation for a weakly shocked meteorite.

[34] The estimated shock pressures by CL spectral deconvolution are concordant with those by refractive index method and Raman spectroscopy, of which the data are based on shock experiments. Recently, the paragenetic assembly of high-pressure phases in some meteorites has been used to estimate shock conditions based on the static experiments [e.g., El Goresy et al., 2010], of which the results are not completely consistent with those obtained from refractive index and Raman spectral measurements. It can be also expected that CL spectroscopy of the samples derived from static experiments provides shock pressures on meteorite and impactite, which might be concordant with the values evaluated using the paragenetic assembly of high-pressure phases. Although it is not yet clear which material as pressure calibration is appropriate to establish a practical shock barometer, CL spectroscopy might have a sufficient potential for quantitative shock estimation in either case.

[35] In this study, the shock reverberation experiment was conducted to induce accurate and reliable shock pressure on the alkali feldspar in the wide pressure range. The total internal energy is, however, lower than that in a single shock loading event which is expected in naturally shocked materials such as meteorite and impactite. Therefore, we must think whether CL of alkali feldspar is dominantly affected by shock pressure or total internal energy. If the intensity at 2.948 eV depends heavily on the total internal energy rather than the shock pressure, it clearly correlates with the first shock pressure in shock reverberation experiment and the correlation gives a shock pressure concordant with the values reported by the previous studies because the first shock step contains most of the total internal energy and entropy in shock reverberation experiment. We used six data set of measured shock velocity (Us) and particle velocity (Up) for oligoclase (density of 2.635 g/cm³) blow 40 GPa [Ahrens et al., 1969], being expressed as Us (km/s) = 3.37 + 1.13 Up (km/s). The first shock pressures are calculated using the impedance match method from these data and the measured impact velocities of projectile as 4.1 GPa for 0.857 km/s, 8.3 GPa for 0.958 km/s, 13.2 GPa for 1.423 km/s, and 16.9 GPa for 1.730 km/s. A plot of the intensity at 2.948 eV...
against the first shock pressure shows a positive linear correlation with a higher gradient than those shown in Figure 6, and allows us to underestimate shock pressures of 14.4 GPa for NWA 2975, 13.1 GPa for Shergotty, 10.9 GPa for Dhofar 019, 10.7 GPa for Zagami, 3.0 GPa for Yamato 000749, and 6.6 GPa for Ries crater. This result suggests that the intensity at 2.948 eV is a function of the peak shock pressure rather than the first shock pressure and the total internal energy. Furthermore, the total internal energy in shock metamorphism might have little influence on CL of alkali feldspar under a given set of conditions, as described below.

Shock process leads to not only shock pressure, but also increasing total internal energy in material, which significantly affects physical features in mineral [Johnson and Cheret, 1998]. A large part of the total internal energy might be used as adiabatic release, a phase transition, formation of shock deformation features, and post-temperature. The present CL spectroscopy of alkali feldspar revealed that the intensity at 2.948 eV is almost independent of mineralogical features such as chemical composition, structural ordering and phase transition in feldspar. Since the shock deformation features locally appear in minerals, they seem to have a limited influence on the CL. According to Sharp and DeCarli [2006], the recovered sample in reverberation-type shock experiment, in the same case as this study, does not reach as high post-temperature as that in single step shock experiment and naturally shocked sample at a shock pressure. The post-temperature effect on CL of the alkali feldspar, therefore, should be discussed here. CL and other luminescence, as well as ESR signals assigned to various types of defect centers in feldspar, have little or no change below a given temperature and totally disappear above it, which have been applied as annihilation temperature for the age determination [e.g., Petrov, 1994; Finch and Klein, 1999; Garcia-Guinea et al., 1999]. A high post-temperature produced by shock metamorphism may give a total elimination of CL signals such as the component at 2.948 eV above the annihilation temperature rather than a change of the intensity depending on temperature. There should be little influence of the post-temperature on CL of the shock-recovered sandine as well as alkali feldspar in the meteorites and the impactite because these feldspar have sufficient CL signals related to the shock-induced defect centers, suggesting a simple usage of CL in alkali feldspar as shock barometer. Also, further works on low shock pressure, static compression, a single shock loading and annealing experiments, as well as high sensitive CL measurements will be necessary for understanding the effects of the total internal energy, post-temperature, rising and shock duration in more detail and improving precision and reliability of shock estimation using CL spectral deconvolution for alkali feldspar.

5. Conclusion

The present CL study on alkali feldspar has revealed that emission intensity of the component at 2.948 eV correlates linearly with peak shock pressure in the range from 4.5 to 40.1 GPa, and that it is almost independent of mineralogical features such as the chemical composition, structural ordering, phase transition, and probably post-temperature produced by shock pressure below 40.1 GPa. The CL spectral deconvolution for alkali feldspar, therefore, provides quantitative and reliable estimation of shock pressure experienced by meteorites and impactites using the linear relation. Furthermore, high-spatial resolution color CL microscopy in the present study visualizes the shock effect on a feldspar grain, and through the studies on distributed feldspar grains provides an isobaric map over the whole rock in meteorite and impactite to interpret how the shockwave traveled during the impact. This shock barometry can be used to clarify the formation process of the impact craters on Earth, Moon, and Mars. Shock pressure estimation on Martian and Lunar meteorites should be progressively helpful for understanding meteoritic and planetesimal collision history, and interpreting the ejection process on Mars and Moon. Additionally, the shock barometer using CL, combined with 39Ar/40Ar chronology, can provide valuable information on detail conditions of collisions during heavy meteoritic bombardment in the early moon without discovery of high-pressure phases as proposed by a pioneer study on lunar meteorite. Finally, CL microscopy and spectroscopy can also aid to understand more about the shock wave mechanics as well as shock stages of different mineral populations in samples from the sample return mission as such as Stardust (Wild-2 comet) and Hayabusa (Itokawa asteroid) for interpretation of their formation and aggregation processes as well.

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